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A PROCESS FOR REMOVING EMULSIONS AND THE  
WRAPPED TARGET COMPONENTS FROM WASTE WATER

TECHNICAL FIELD

5 The invention pertains to the general field of  
waste water treatment processes and, more particularly,  
to a process for removing oil-in-water emulsions from  
waste water. The process limits the emulsions from  
breaking up. Thus, reducing the target components  
10 wrapped within the emulsions from being released and  
entering the water phase.

BACKGROUND ART

15 An oil-in-water emulsion is a solution consisting  
of small oil particles that are evenly dispersed in  
water. The emulsion can be stabilized by adding  
surfactant compounds, which bridge nonpolar oil and  
polar oil water phases. One method of treating waste  
that is created by the emulsion is to break up the  
emulsion's state using a de-emulsifier. The  
de-emulsifier utilizes chemicals which separate the  
20 oil-in-water emulsion into an oil phase and a water  
phase, thus allowing both the oil and the water to be  
recycled.

25 A disadvantage of breaking up an emulsion is that  
some relatively high water soluble compounds, which  
were originally in the oil particles, may be  
re-distributed to the water phase. Additional  
treatment is then required if the concentration of the  
water soluble compounds exceeds a pre-imposed discharge  
limit.

One example in which waste water is generated is during the manufacturing of propofol injectable. Propofol is chemically described as 2,6-Diisopropylphenol (CAS registration number 2078-54-8) and has been widely used as anesthesia. Propofol injectable is formulated in a white, oil-in-water emulsion. The final concentration of propofol injectable that pharmaceutical companies make is 1%. In addition to the active component propofol, the formulation also contains 10% soybean oil, 2.25% glycerol, 1.2% egg lecithin and 0.005% disodium edetate with sodium hydroxide to adjust pH to 7 - 8.5.

The waste water generated during the manufacturing of propofol injectable contains white emulsion of propofol, soybean oil, glycerol, egg lecithin and a small amount of disodium edetate. Since propofol is a phenolic compound, and soybean oil belongs to oil waste, their discharge in the United States is regulated by a governmental agency. For many cities in the U.S., the permissible discharge limit for phenolic compounds is 0.5 mg/L, and for oil is 375 mg/L. Since the concentrations of propofol and soybean oil are more than 10,000 times higher than the discharge limits, the waste water generated during pharmaceutical production of propofol injectable requires treatment to remove or reduce propofol and soybean oil from the waste water before being discharged into a sewage system.

Propofol is a very stable phenolic compound. Stress tests have shown no detectable degradation when 3% propofol is refluxed for 2 hours in one NHCL solution, or refluxed for 2 hours in 7%  $H_2O_2$  solution, or under 3 hours of UV radiation at 254 nm. Therefore, it is difficult to chemically destroy propofol emulsion. If a de-emulsifier is added to the waste, propofol molecules originally wrapped by lecithin will be released into the water phase, thus resulting in a

propofol-saturated water phase that is higher than the discharge limit.

A search of the prior art did not disclose any patents that read directly on the claims of the instant invention, however the following U.S. patents are considered related:

	<u>PATENT NO.</u>	<u>INVENTOR</u>	<u>ISSUED</u>
	5,433,853	Mamone	18 July 1995
	4,160,742	Raman	10 July 1979
10	4,075,183	Kawakami, et al	21 February 1978
	4,026,794	Mauceri	31 May 1977
	3,956,117	Bradley, et al	11 May 1976

The 5,433,853 patent discloses the use of an acid, a coagulant, and a flocculent to remove emulsified oils, dissolved solids, and particulates from wastewater. The wastewater is pH adjusted to approximately 6 by an acid. Chemical coagulant (such as ferric chloride, aluminum chloride) is added to remove oil and particulates by means of precipitation. The pH of the water is re-adjusted to about 6 so that the metal hydroxides are dissolved, causing the oil, grease and other constituents to be separated from the liquid phase as a solid. A polymer flocculent is added in the last stage to cause an attraction between the solids allowing them to gather and build mass. A vertical plate pack chamber facilitates the removal of the flocculants.

The 4,160,742 patent discloses the use of copolymers of acrylamide and methyacrylamidopropytri-methylammmonium chloride to de-emulsify oil-in-water emulsions especially in waste streams prior to their discharge from petroleum refineries, industrial plants and the like.

The 4,075,183 patent discloses a water-soluble, cationic high polymer consisting of (A) at least one of acrylamide and methacrylamide and (B) at least one of

ammonium type monomers of either one of the formulas:  
 ##STR1## wherein R.sub.1 is a hydrogen atom or a methyl  
 group, R.sub.2 and R.sub.3 are each a lower alkyl  
 group, R.sub.4 is a hydrogen atom, a lower alkyl group,  
 5 an aryl group, a hydroxy (lower) alkyl group, a benzyl  
 group or a group of the formulas: CH.sub.2  
 COO(CH.sub.2).sub.m CH.sub.3 (m being an integer of 0  
 or 1), R.sub.5.sup.- is a group of either one of the  
 formulas: --(CH.sub.2).sub.2 COO.sup.- and  
 10 -(CH.sub.2).sub.3 SO.sub.3.sup.-, X is a halogen atom  
 or an acid residue, Y is -O- or --NH-- and n is an  
 integer of 1 to 4, a process which initiates the  
 polymerization of the monomeric component (A) with or  
 without a portion of the monomeric component (B) in an  
 15 aqueous medium containing an organic solvent selected  
 from the group consisting of acetone, acetonitrile,  
 t-butanol, tetrahydrofuran and dioxane at a  
 concentration of about 15 to 70% by weight until the  
 polymerization proceeds to a certain extent and then  
 20 continuing the polymerization while adding the  
 remaining portion of the monomeric component (B)  
 thereto under the occasional supplementation of a  
 water-miscible organic solvent thereto so as to keep an  
 appropriate viscosity of the reaction system to produce  
 25 the high polymer in a high yield with ease.

The 4,026,794 patent discloses the use of a water  
 soluble amphoteric metal, such as MgCl<sub>2</sub> and ZnCl<sub>2</sub>, and a  
 water soluble cationic terpolymer to break the  
 negatively charged oil-in-water emulsion to form an  
 30 easily recoverable floc containing oil particulates  
 from the wastewater.

The 3,956,117 patent discloses a method of breaking  
 oil-in-water emulsions involving treating such  
 oil-in-water emulsions with a polycationic  
 35 water-soluble condensation copolymer. Treatment with  
 the copolymer transforms the emulsified oil particles

into flocs which may be directly removed or which may be removed after the addition of one or more flocculants.

The above prior art patents address separation and removal of oil, greases and particulates in the oil-in-water emulsions. However, these patents were not designed to keep the components originally wrapped in the emulsion from entering the water phase. Such a need is often found in pharmaceutical products where the active pharmaceutical ingredient(s) inside the oil-in-water emulsion is often much more toxic than the oil phase. A wastewater treatment process must, therefore, not only separate the oil but also separate the compounds inside the emulsion from the water phase.

## DISCLOSURE OF THE INVENTION

A process for removing oil-in-water emulsions and the target components wrapped within the emulsions from waste water that results from the production of a water-based product, the process comprising the following steps:

- a) collect the emulsion waste water in a container,
- b) add a quantity of a precipitation reagent with trivalent cations, and
- c) add a quantity of a base compound to adjust the pH of the waste water to approximately 6.5, which converts the dissolved trivalent cations to gelatinous cation hydroxide precipitation and separates the emulsion and the target components from the waste water, and

d) separate the precipitation from the waste water by utilizing a filtration means.

To refine the above process, the precipitation can be separated from the waste water by utilizing a  
5 filtration means. The filtration means can consist of several processes including: vacuum filtration, positive pressure filtration, or by using a centrifuge.

By using the above process, the level of an emulsion can be reduced from 1000 ppm or above to less  
10 than 1 ppm. In addition, target components wrapped in the emulsion remain in the flocs, which allows the treated water to meet the disposal limits.

In view of the above disclosure, the primary object of the invention is to provide a process by which  
15 waste water containing an oil-in-water emulsion may be treated to remove the emulsion, along with the components inside the emulsion thus allowing proper disposal of the waste water.

It is also an object of the invention to:

- 20 o provide a waste water treatment process that can be utilized to treat different types of substances containing an oil-in-water emulsion,
- o provide a waste water treatment method that is quickly and easily performed,
- 25 o allow the amounts of certain chemicals within waste water to be determined, and
- o provide a process by which a person/corporation who manufacture products having waste water can dispose of the waste water according to  
30 government-specified levels.

These and other objects and advantages of the present invention will become apparent from the subsequent detailed description of the preferred embodiment and the appended claims.

## BEST MODE FOR CARRYING OUT THE INVENTION

The best mode for carrying out the invention is presented in terms of a preferred embodiment for preparing (treating) waste water containing oil-in-water emulsion for disposal. The amount of oil-in-water emulsion that can be discharged during disposal without treatment is regulated by most United States city's municipal water districts. Typically, the permissible discharge limit for a phenolic compound is 0.5 mg/L, and for oil it is 375 mg/L. Since the concentrations of certain products, such as Propofol injectable and soybean oil, are more than 10,000 times higher than the discharge limits allowed, the waste water created during manufacture must be treated prior to disposal.

In order to treat the waste water/emulsion solution, (hereinafter "WWES"), the instant invention utilizes an aluminum hydroxide co-precipitation method. In this method a specified amount of a precipitation reagent having trivalent compounds, such as potassium aluminum sulfate ( $KAl(SO_4)_2$ ), aluminum chloride or ferric chloride is added along with a determined amount of a base compound, such as sodium bicarbonate ( $NaHCO_3$ ), sodium carbonate, ammonia or sodium hydroxide. The base compound is used to adjust the pH level, precipitation is generated within the WWES. (Note: for the purpose of this description, the precipitation reagent having trivalent compounds will be referred to throughout the text as potassium aluminum sulfate). The precipitation then brings down suspended oily particles (the "emulsion") and limit the emulsion from breaking up. Thus, molecules that were originally wrapped in the oily particles are retained in the sediments, rather than distributed between oil and water phases according to their solubilities in



both phases.

In order to use the invention, the following process is utilized:

A specified amount of potassium aluminum sulfate  
 5 (KAl(SO<sub>4</sub>)<sub>2</sub>) is added to a container having an amount of  
 WWES within. The potassium aluminum sulfate changes the  
 pH of the WWES from neutral to about 3.5. The pH is  
 then adjusted to approximately 6.5 by adding the base  
 compound. As the pH increases, dissolved aluminum ions  
 10 hydrolyse to form gelatinous aluminum hydroxide  
 (Al(OH)<sub>3</sub>) precipitate. The gelatinous aluminum  
 hydroxide (Al(OH)<sub>3</sub>) precipitate slowly settles to the  
 bottom of the container, taking the suspended emulsions  
 and the wrapped target components with it, thus  
 15 creating a clear water phase and a settlement phase.  
 The clear water is then separated from the settlement  
 by a filtration means, that can consist of vacuum  
 filtration, positive pressure filtration, a centrifuge,  
 or by utilizing a filter paper, such as a No. 6 Whatman  
 20 filter paper. In order to facilitate a complete phase  
 separation in certain products, an activated carbon  
 layer is used with the filter paper which is typically  
 comprised of a #6 Whatman paper.

In order to disclose a complete description and the  
 25 use of the invention, the following examples are given:

Example #1, treatment of 1% Propofol injectable

Example #2, treatment of diluted Propofol  
 injectable,

Results of Examples #1 and #2

30 Example #3, regular Milk

Example #4, reduced fat milk

Example #5, fat free milk

Example #6, soy milk

Example #7, Ensure<sup>(R)</sup> nutritional drink produced by  
 35 Ross Products Division, Abbott Laboratories, Columbus,  
 OH, 43215

The instant invention is designed to treat emulsion waste waters in examples 1 and 2 where separation of oil as well as propofol is required. It is important to limit emulsions from breaking up so the wrapped  
 5 target components remain in the emulsions to allow separation, instead of entering the water phase. Examples 3 - 7 are demonstrations that this invention is also applicable to other matrices.

Example 1. Treatment of 1% Propofol Injectable

10 To a solution of 1% Propofol injectable, add 5% (by weight) of potassium aluminum sulfate, hereinafter  $KAl(SO_4)_2$ . For example, 5 grams of  $KAl(SO_4)_2$  should be added to 100 grams of 1% Propofol injectable solution. Once the  $KAl(SO_4)_2$  has been completely dissolved, the  
 15 pH of the solution will be approximately 3.5.

While stirring the solution, slowly add solid sodium bicarbonate ( $NaHCO_3$ ) until the pH rises to 6.5. The amount of sodium bicarbonate needed to achieve the designated pH is about 3 - 5% weight of the solution.  
 20 Since sodium bicarbonate is a weak base, the pH of the solution won't be greater than 7, even if more than 5% of sodium bicarbonate is used.

As the pH of the solution increases, the dissolved aluminum ions ( $Al^{+3}$ ) start to precipitate as a form of  
 25 glutinous aluminum hydroxide ( $Al(OH)_3$ ). The aluminum hydroxide also absorbs the emulsion in the solution while precipitating, thus resulting in phase separation of clear water at the top and white precipitation at the bottom. It should be noted that due to the  
 30 generation of carbon dioxide, the precipitation first is on the top layer. If it is left standing overnight, all precipitation will be settled at the bottom layer.

The addition of sodium bicarbonate generates carbon dioxide bubbles, and care should be taken to add sodium

free milk of 6,2000 NTU, the turbidity reduction by this treatment is 12,000 times.

#### Example 6. Soy milk

To a solution of 100 mL soy milk (Tan Nam), 2.5 gram of  $KAl(SO_4)_2$  is added. The resulting pH of the solution is 3.75. Slowly add 1.5 gram of  $NaHCO_3$  while stirring; phase separation starts when the aluminum hydroxide starts to precipitate. The resulting precipitates are then filtered through a No. 6 filter paper. The Turbidity of the final filtrate is 1.4 NTU. About 30 grams of solids remained on the filter paper. The turbidity of original soybean milk is 29,000 NTU, thus Turbidity is reduced by 20,000 times.

EPA method 413.2 is used to measure oil and grease level. The oil and grease level in the soy milk is 43,000 mg/L. After treatment, oil and grease level is reduced to 10 mg/L.

#### Example 7. Ensure<sup>(R)</sup> Nutritional drink

Prepare a starting solution by adding 10 gram of the Ensure<sup>(R)</sup> nutrition drink into 90 mL of water. Add 2 grams of  $KAl(SO_4)_2$ , the resulting pH is 3.56. Slowly add 1.5 grams of  $NaHCO_3$  while stirring; phase separation starts when the aluminum hydroxide starts to precipitate. The resulting precipitates are then filtered through a No. 6 filter paper. The Turbidity of the final filtrate is 0.27 NTU. Compared with the Turbidity of 10 times diluted ensure solution of 99,500 NTU, the turbidity reduction by this treatment is 300,000 times.

Zeta potential analysis